



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : C03C 17/42, C09K 3/18	A1	(11) International Publication Number: WO 98/40323 (43) International Publication Date: 17 September 1998 (17.09.98)
(21) International Application Number: PCT/JP98/01001 (22) International Filing Date: 11 March 1998 (11.03.98) (30) Priority Data: 9/56342 11 March 1997 (11.03.97) JP (71) Applicant: NIPPON SHEET GLASS CO., LTD. [JP/JP]; 5-11, Dosho-machi 3-chome, Chuo-ku, Osaka-shi, Osaka 541-0045 (JP). (72) Inventors: YAMAMOTO, Hiroaki; Nippon Sheet Glass Co., Ltd., 5-11, Dosho-machi 3-chome, Chuo-ku, Osaka-shi, Osaka 541-0045 (JP). KOBAYASHI, Hiroaki; Nippon Sheet Glass Co., Ltd., 5-11, Dosho-machi 3-chome, Chuo-ku, Osaka-shi, Osaka 541-0045 (JP). TERAN- ISHI, Toyoyuki; Nippon Sheet Glass Co., Ltd., 5-11, Dosho-machi 3-chome, Chuo-ku, Osaka-shi, Osaka 541-0045 (JP). SUNADA, Takashi; Nippon Sheet Glass Co., Ltd., 5-11, Dosho-machi 3-chome, Chuo-ku, Os- aka-shi, Osaka 541-0045 (JP). KAMITANI, Kazutaka; Nippon Sheet Glass Co., Ltd., 5-11, Dosho-machi 3-chome, Chuo-ku, Osaka-shi, Osaka 541-0045 (JP). (74) Agent: KOYAMA, Yuu; Yotsuya-takagi Building, 2nd floor, 9, Yotsuya 2-chome, Shinjuku-ku, Tokyo 160-0004 (JP).		(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, HU, IL, IS, JP, KE, KG, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, TJ, TM, TR, TT, UA, UG, UZ, VN, YU, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG). Published <i>With international search report.</i> <i>Before the expiration of the time limit for amending the</i> <i>claims and to be republished in the event of the receipt of</i> <i>amendments.</i>
(54) Title: A SUBSTRATE HAVING A TREATMENT SURFACE		
(57) Abstract <p>For obtaining a substrate on the surface of which a water repellent film is firmly bonded through an undercoating film, and which shows a low critical inclination angle, superior durability, and high density, a water repellent and/or oil repellent film layer is formed by using a liquid for undercoating treatment. The liquid for undercoating treatment is obtained by dissolving and reacting a material having chlorosilil radical in molecular form therein and is dissolved into an alcohol group solvent, so that a surface roughness (Ra) of less than 0.5 nm is obtained, thereby achieving high durability and a low critical inclination angle.</p>		

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece	ML	Mali	TR	Turkey
BG	Bulgaria	HU	Hungary	MN	Mongolia	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MR	Mauritania	UA	Ukraine
BR	Brazil	IL	Israel	MW	Malawi	UG	Uganda
BY	Belarus	IS	Iceland	MX	Mexico	US	United States of America
CA	Canada	IT	Italy	NE	Niger	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NL	Netherlands	VN	Viet Nam
CG	Congo	KE	Kenya	NO	Norway	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NZ	New Zealand	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	PL	Poland		
CM	Cameroon	KR	Republic of Korea	PT	Portugal		
CN	China	KZ	Kazakstan	RO	Romania		
CU	Cuba	LC	Saint Lucia	RU	Russian Federation		
CZ	Czech Republic	LI	Liechtenstein	SD	Sudan		
DE	Germany	LK	Sri Lanka	SE	Sweden		
DK	Denmark	LR	Liberia	SG	Singapore		
EE	Estonia						

DESCRIPTION

A SUBSTRATE HAVING A TREATMENT SURFACETECHNICAL FIELD

5 The present invention relates to a substrate of glass, ceramics, plastic, or metal, etc., having a treatment surface, i.e., a water repellent coating or film being formed on an undercoating layer or film thereof, and a treatment method therefor.

BACKGROUND ART

10 Conventionally, a substrate comprising for example glass or the like, on the surface of which a water repellent coating, layer or film is formed, has been already known, in for example, Japanese Patent
15 Publication No. Hei 4-20781 (1992), Japanese Laid-open Patent No. Hei 5-86353 (1993), Japanese Laid-open Patent No. Hei 5-161844 (1993), Japanese Laid-open Patent No. Hei 2-311332 (1990) and Japanese Patent No. 2,525,536.

20 In Japanese Patent Publication No. Hei 4-20781 (1992), it is disclosed that on the surface of the substrate there is formed a coating layer or film from a silane compound excluding polyfluoro radical or synthetic resin, and further thereon is formed a water repellent

and oil repellent multi-layer coating or film comprising a silane compound including polyfluoro radical.

Further, in Japanese Laid-open Patent No. Hei 5-86353 (1993), there is disclosed a method by which a thin film
5 of siloxan radical is formed on the surface of glass, ceramics, plastic, or metal, etc., by use of a compound including chlorosilil radical, such as SiCl_4 , in molecular form thereof, and further thereon is formed a chemical absorption unimolecular accumulation layer or
10 film (a water repellent film or coating).

Also in Japanese Laid-open Patent No. Hei 5-161844 (1993), there is described a method in which, having formed a unimolecular film of siloxan radical or an absorption film of polysiloxan previously, the chemical
15 absorption unimolecular accumulation film (a water repellent film or coating) is formed on the surface of a substrate by a further chemical absorption processing conducted in an atmosphere including a surface-active agent of chlorosilane radical.

Moreover, Japanese Laid-open Patent No. Hei 2-311332 (1990) describes a water repellent glass obtained through sililating the surface of glass substrate by a silil compound, such as fluorinated alkylsilane, the surface of which is formed from a metal oxide, such as SiO_2 .

Furthermore, Japanese Patent No. 2,525,536 discloses that an undercoating film or layer of silica is applied on the glass substrate before treating the surface thereof by the fluorine compound, in the same manner as described in Japanese Laid-open Patent No. Hei 2-311332
30 (1990), and further that weather resistance of the water repellent film is improved by including olefin telomer in the fluorine compound.

With the substrate which can be obtained by the method disclosed in Japanese Patent Publication No. Hei 4-20781 (1992), since the density of the undercoating layer is low, the undercoating layer must be more than
5 100 nm in thickness thereof and also the temperature for baking must be higher than 400°C.

In the method disclosed in Japanese Laid-open Patent No. Hei 5-86353 (1993), since the absorbent for the reaction with water treatment in air is unstable, it is
10 necessary to maintain the humidity in the atmosphere low, thereby control of the environment being difficult. Further, there are problems, in that it takes 2-3 hours for the treatment, and the nonaqueous solvent is expensive.

15 For implementation of the method which is disclosed in Japanese Laid-open Patent No. Hei 5-161844 (1993), equipment for controlling the atmosphere must be large-scaled, and it takes time to form a perfect absorption film.

20 With the substrate which is obtained by the method disclosed in Japanese Laid-open Patent No. Hei 2-311332 (1990), since baking at 500°C for instance is necessitated for obtaining the high density metal oxide layer when forming the metal oxide film through a sol-gel
25 method, also large-scaled equipment for baking the substrate at high temperature is necessary, thus raising the production cost. Further, having tried this method, the roughness of the metal oxide film thereby obtained is relatively high, resulting that it is difficult for water
30 drops present on the surface of the water repellent glass to roll freely thereon.

Furthermore, with the substrate which is obtained by the method disclosed in Japanese Patent No. 2,525,536, though being superior with respect to weather resistance, such a result is only obtained through double-checking
5 thereof that the durability of the water repellent film in a friction test is adequate, and it is also difficult for water drops present on the surface of the water repellent glass to roll freely thereon since the roughness of the surface of the silica undercoating layer
10 or coating is relatively high.

DISCLOSURE OF THE INVENTION

For resolving the drawbacks in the conventional art mentioned above, according to the present invention, there is provided a substrate having a treatment surface,
15 characterized in that, on a surface of a substrate of glass, ceramics, plastics or metal, an undercoating film layer is formed by drying a liquid for undercoating treatment which is obtained by dissolving and reacting a materiel having chlorosilil radical in molecular form
20 therein within an alcohol group solvent, so that on said undercoating film layer there is formed a water repellent or oil repellent layer, wherein a surface roughness (Ra) of said surface layer is equal to or less than 0.5 nm.

Further, the surface roughness (Ra) of the surface
25 layer is preferably to be as small as possible. However, for example, the surface roughness (Ra) of a fire polished surface of float glass (i.e., upper surface of the float glass floating on molten tin) is about 0.2 nm, and the roughness (Ra) of a glass surface obtained
30 through precise grinding is about 0.1 nm. Therefore, the substantially lowest threshold value of surface roughness

(Ra) of the glass surface which can be obtained is about 0.1 - 0.2 nm.

As mentioned above, the undercoating film or layer formed from the undercoating treatment liquid, which is
5 obtained by dissolving and reacting the material having chlorosilil radical in molecular form therein, has high smoothness, and therefore, the surface layer formed on the undercoating film or layer also comes to have high smoothness ($Ra \leq 0.5$ nm), reflecting the smoothness of
10 the undercoating layer, thereby obtaining a superior water repellent property, i.e., a high contact angle and a low critical inclination angle.

Here, it is possible to remove defects in appearance by keeping the surface of the substrate clean when
15 forming the undercoating layer or film on it, and it is also possible to increase adhesive strength between the substrate surface and the undercoating film by activating the surface of the substrate. For example, even in a case where the glass substrate comprises an oxide, it is
20 possible to form an active surface by grinding the surface to within $0.5 \text{ nm} \leq Ra \leq 3.0 \text{ nm}$ using a grinding agent.

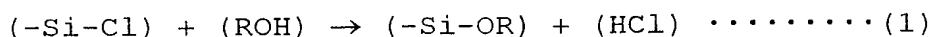
However, in the case where the roughness (Ra) of the substrate surface exceeds 3.0 nm, it is difficult to make
25 the roughness (Ra) of the surface layer (the water repellent layer) less than 0.5 nm even if effecting the undercoating treatment thereon. Therefore, it is preferable that the roughness (Ra) of the substrate surface be equal to or less than 3.0 nm. Moreover, when
30 the substrate is made of glass plate, transparency of the substrate can be maintained when the roughness (Ra) is within a range of $0.5 \text{ nm} \leq Ra \leq 3.0 \text{ nm}$.

Further, in the case where hydrophilic radical is poor in the surface of the substrate, it is preferable to conduct the surface treatment after treatment for hydrophilizing the surface, i.e., by treating the surface
5 with plasma containing oxygen or treating under a corona discharge atmosphere, or alternatively, by irradiating ultraviolet light of a wavelength in the vicinity of from 200 to 300 nm onto the substrate surface in an atmosphere containing oxygen.

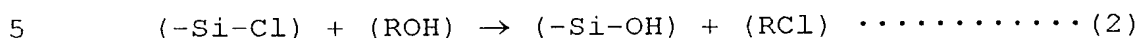
10 Further, according to the present invention, it is appropriate to restrict the concentration of the material having chlorosilil radical in molecular form therein within the liquid for the undercoating treatment, this being equal to or greater than 0.01 wt% and equal to or
15 less than 3.0 wt%.

As an example of a material having chlorosilil radical in molecular form therein, there can be listed SiCl_4 , SiHCl_3 or SiH_2Cl_2 , etc., and it is possible to select a single or a plurality of materials from among
20 these as the material. In particular, since it contains the most Cl radicals, SiCl_4 is preferable. The chlorosilil radical is very high in reactivity thereof, and it forms a minute or dense undercoating film through a self-condensation reaction or by reaction with the
25 substrate surface. However, it can contain a material in which a part of a hydrogen radical is replaced by methyl radical or ethyl radical.

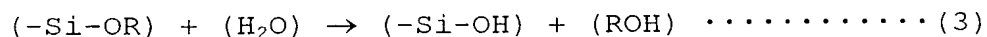
Further, as the alcohol group solvent, for example, methanol, ethanol, 1-propanol, and 2-propanol are
30 desirable. The material containing chlorosilil radical in molecular form therein and the alcohol group solvent, as is shown by equation (1) below, react to form alkoxide by removing hydrogen chloride:



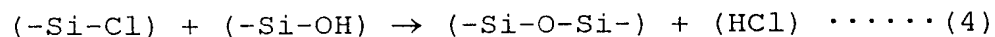
Further, the material containing chlorosilil radical in molecular form therein and the alcohol group solvent react as shown by equation (2) below:



In the alcohol solvent, a part of $(-\text{Si}-\text{OR})$ reacts as shown by equation (3) below with an acidic catalyst which is formed as shown by equation (1), and forms $(-\text{Si}-\text{OH})$.



10 In addition, $(-\text{Si}-\text{OH})$ which is produced as shown by the above equations (2) and (3) reacts as shown by equation (4) below, and forms siloxane bonding:



15 It is considered that, by means of the above-mentioned siloxane bonding, the bonding between the substrate and the undercoating film, or between the undercoating film and the surface film such as the water repellent film is strengthened. Namely, in the case where a compound including the siloxane bonding is simply
20 used as the liquid for the undercoating treatment as disclosed in the conventional arts, though the siloxane bonding exists within the undercoating film, the siloxane bonding joining between the substrate and the undercoating film, or between the undercoating film and
25 the water repellent film, are not so influential.

According to the present invention, by treating with a liquid for performing an undercoating treatment which is obtained by reacting the materiel having chlorosilil radical in molecular form in the alcohol group solvent

within thirty (30) minutes after mixing thereof, an undercoating film being superior in smoothness can be formed, and since a part of the chlorosilil radical takes part in the siloxane bonding, good bonding between the substrate and the water repellent film can be obtained by the siloxane bonding.

Here, it is preferable that the concentration of the material having chlorosilil radical in molecular form therein contained in the undercoating treatment liquid, though depending on the method of coating, be equal to or greater than 0.01 wt% and equal to or less than 3.0 wt%. If it is lower than that, no effect by adding the material can be obtained, and if higher than that, the effect of adding the material is not improved. For example, in particular, in the case of coating by using, for example, a curtain flow coating method, judging from the appearance during the coating, it is preferable that the concentration be equal to or greater than 0.03 wt% and equal to or less than 1.0 wt%.

The method for coating the undercoating treatment liquid should not be limited in particular. However, other methods can be listed, such as: a dip coating method, a curtain flow coating method, a spin coating method, a bar coating method, a roll coating method, a hand coating method, a brush painting method, a spray coating method, etc.

Further, as the surface treatment, for instance, a water repellent treatment and an oil repellent treatment can be listed. Though the liquid agents for the water and oil repellent treatments should not be limited in particular, a treating method by using water repellent or oil repellent agents containing silane compound, siloxane compound or silicon compound therein is preferable.

As the silane compound, there can be listed water repellent agents containing:

- 5 $\text{CF}_3(\text{CF}_2)_7(\text{CH}_2)_2\text{Si}(\text{OCH}_3)_3$,
 $\text{CF}_3(\text{CF}_2)_6(\text{CH}_2)_2\text{Si}(\text{OCH}_3)_3$,
 $\text{CF}_3(\text{CF}_2)_7(\text{CH}_2)_2\text{SiCl}_3$,
 $\text{CF}_3(\text{CF}_2)_6(\text{CH}_2)_2\text{SiCl}_3$, and the like.

10 These repellent agents can be used, depending on necessity, by being hydrolyzed using a catalyst such as acid or hydrochloric acid. Further, an agent, containing the siloxane compound which can be obtained through hydrolysis or condensation of the silane compound, can be used too.

15 As the silicon compound there can be used polydimethylsiloxane of straight chain or chain form, or silanol metamorphism, hydrogen metamorphism, halogen metamorphism thereof, etc.

20 For the method for the water repellent or oil repellent treatment, in the same manner as the undercoating treatment, though it should not be limited in particular, methods such as the hand coating method, the brush painting method, etc., can be applied thereto.

25 Further, as the surface treatment according to the present invention, a hydrophilic treatment or an antifogging treatment can be applied, in addition to the water repellent or oil repellent treatment.

DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

Hereinafter, detailed explanation of the embodiments according to the present invention will be given.

(Embodiment 1)

By adding 0.01 g of chlorosilane (SiCl_4 , produced by Shinnetsu Silicon Co.) to 100 g of ethanol (produced by Nakaraitekusu Co.) and mixing thereof, a liquid for the undercoating treatment is obtained. The obtained liquid
5 for the undercoating treatment was coated on a glass plate (300×300 mm) which was ground and cleaned, under a humidity of 40% and at room temperature, and was then dried for about one minute, thereby obtaining the undercoating film.

10 Then, by dissolving 1.3 g of $\text{CF}_3(\text{CF}_2)_7(\text{CH}_2)_2\text{Si}(\text{OCH}_3)_3$ (heptadecafluorodesiltrimethoxysilane, produced by Toshiba Silicon Co.) into 40.6 g of ethanol and mixing them for an hour, and thereafter by adding 0.808 g of ion-exchanged water and 0.1 N of hydrochloric acid and
15 mixing them for a further one hour, an agent a for the water repellent treatment was obtained.

Thereafter, 0.3 ml of agent a for the water repellent treatment was put onto a cotton applicator and it was coated onto the glass substrate with a film formed by the
20 undercoating treatment, and thereafter any agent for water repellent treatment which was excessively coated is removed by wiping with a fresh cotton applicator soaked in ethanol, thereby obtaining a water repellent glass substrate.

25 The contacting angle with water drops of 2 mg in size was measured as a static contact angle by using a contact goniometer (CA-DT, produced by Kyowa Kaimen Kagaku Co.).

As a weather resistance test, ultraviolet light was irradiated there onto by using Super UV tester (W-13,
30 produced by Iwasaki Denki Co.), under the conditions of an ultraviolet light strength of 76 ± 2 mW/cm², irradiating for 20 hours with a darkness cycle of 4

hours, and by showering the substrate with ion-exchanged water for 30 seconds every hour.

Further, as an abrasion test, a sand-rubber eraser (product by Lion Co., No. 502) was rubbed on the water repellent glass reciprocally 100 times at a load of 50 g per 15 × 7 sq. mm.

Moreover, as a measure for indicating the water repellency, the critical inclination angle was measured. For measuring the performance of rolling a water drop on the surface of the water repellent glass (contact angle = 100 - 110°), a water drop of diameter 5 mm (it comes to be approximately semicircular in shape if the contact angle is 100 - 110°) was disposed on the surface of the water repellent glass which is horizontally positioned. Then, the water repellent glass plate was inclined gradually, and the inclination angle (the critical inclination angle) when the water drop disposed on the surface of the water repellent glass begins rolling was recorded. The smaller the critical inclination angle, the better in dynamic repellent property. For instance, this applies to rain drops landing on the front windshield glass of a moving automobile which must be easily splashed or scattered away so that they do not interrupt the view of the driver.

However, as the smoothness of the obtained water repellent glass, the surface roughness (Ra), is calculated by measuring the surface contour with an atomic force microscope (SPI3700, produced by Seiko Electronics Co.) by a cyclic contact mode.

As shown in TABLE 1, an initial contact angle was 108°, an initial critical inclination angle 13°, and the contact angle after the weather resistance test of 400

hours was 88°, and that after the abrasion test is 84°, serving as a measure of the durability thereof.

(Comparison 1)

5 A water repellent glass substrate was obtained in the same manner as in embodiment No. 1, except that 0.005 g (0.005 wt%) of chlorosilane was added in the preparation of the liquid for the undercoating treatment.

10 As shown in TABLE 1, though an initial contact angle of 107° is indicated, the initial inclination angle is large, at 18°, and the contact angle after the weather resistance test came down to 71°, thereby indicating that the durability is reduced.

(Examples 2 to 4 and Comparison 2)

15 Water repellent glass substrates were obtained in the same manner as in embodiment No. 1, except that 0.5 g, 1.0 g, 3.0 g and 5.0 g (0.5 wt%, 1.0 wt%, 3.0 wt% and 5.0 wt% in concentration) of chlorosilane were added to the respective preparations of the liquid for the undercoating treatment.

20 When the concentration of chlorosilane is high, the thickness of the undercoating becomes thick, and as a result of this, the interference of light is gradually strengthened. When it exceeds 5 wt% in concentration thereof, a remarkable increase in color reflection can be distinguished. When the concentration of chlorosilane rises further so as to increase the thickness of the undercoating layer, a baking process is additionally required.

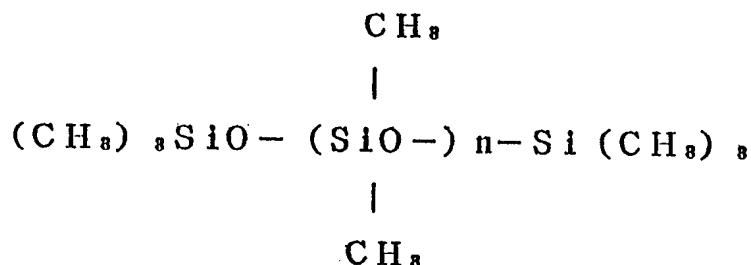
(Example 5)

In a 1 liter glass reactor having a thermometer, a mixer and a cooler, 10.0 g of polydimethylsiloxane containing hydrolysis radical, which is expressed by the chemical equation shown below, was reacted with 1.0 g of

5 $\text{CF}_3(\text{CF}_2)_7(\text{CH}_2)_2\text{Si}(\text{OCH}_3)_3$ (heptadecafluorodesiltrimethoxysilane, produced by Toshiba Silicon Co.) together with 360 g of t-butanol and 0.1 N of hydrochloric acid in a co-hydrolysis reaction for 5 hours at a temperature of 80°C, and further 160 wt% of n-hexane was added and mixed

10 for 10 hours at room temperature.

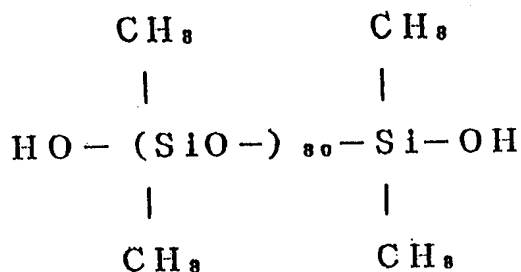
[Chemical Equation 1]



Further, by adding 10.0 g of organopolysiloxane which is expressed by the chemical equation shown below and 5.0

15 g of methasulfonic acid into the mix and mixing them for 10 minutes, an agent b for the water repellent treatment was obtained.

[Chemical Equation 2]



By coating the agent for water repellent treatment on the undercoated glass substrate which was produced at a 0.5 wt% concentration of SiCl_4 , in the same manner as in embodiment 1, a water repellent glass substrate was
5 obtained.

Also with this repellent glass substrate, as shown in the TABLE 1, superior results can be obtained in the initial contact angle and the durability (i.e., the weather resistance test and the abrasion test).

10 (Comparisons 3 and 4)

After the undercoating treatment using tetrachlorotinstan or tetrachloro as the agent for the undercoating treatment in place of chlorosilane, the water repellent glass substrate was produced by using the
15 above-mentioned agent b for water repellent treatment thereof.

Though they show 106° for the initial contact angle, however, the initial critical inclination angles thereof became large, such as 18° and 19° , and the contact angles
20 after the weather resistance test were reduced to 65° and 64° , respectively.

(Comparison 5)

The water repellent glass substrate was produced in the same manner as in embodiment 1 except that as the
25 solvent for the undercoating treatment liquid, chloroform was used in place of ethanol.

Though TABLE 1 shows a large contact angle at 107° , however, the initial critical inclination angle is large, such as 20° , and the contact angle after the weather

resistance test was reduced to 63° and the contact angle after the abrasion test was also reduced to 67°.

(Comparison 6)

Comparison 6 was performed for double-checking
5 embodiment 6 which is disclosed in the specification of Japanese Patent No. 2,525,536.

Namely, the water repellent glass substrate was obtained in the same manner as in embodiment 1 except that as the solvent for the undercoating treatment liquid
10 perfluorocarbon solution (FC-77, produced by 3M Co.) was used in place of ethanol.

The results show a high value for the surface roughness (Ra) at 7.0 nm, and also a high value for the initial critical inclination angle at 25°. Also, though
15 it shows the initial contact angle at 107°, the contact angle thereof after the abrasion test was reduced to 65°.

(Comparison 7)

Comparison 7 was performed for double-checking
20 embodiment 3 which is disclosed in Japanese Laid-open Patent No. Hei 2-311332 (1990) cited above as the prior art.

Namely, dissolving and mixing 31 g of
tetraethylsilicate (produced by Colcoat Co.) into 380 g
25 of ethanol while adding 6.5 g of water and 1.6 g of 1N hydrochloric acid, and waiting for 24 hours at a temperature of 20°, the liquid for the undercoating treatment was prepared.

This liquid for the undercoating treatment was
30 painted by the flow coating method in the same manner as

in embodiment 1 and was dried in about a minute. After the undercoating treatment, a layer of silicon oxide was formed through a heating process by heating the substrate for an hour. Thereafter, the water repellent glass substrate was obtained by using the above-mentioned agent
5 a for the water repellent treatment, in the same manner as in embodiment 1.

The surface roughness (Ra) shows a high value at 0.6 nm, and the initial critical inclination angle is also
10 high, at 22°. The contact angle was 107°, however, it went down to 67° after the abrasion test.

(Comparison 8)

The water repellent glass substrate was obtained in the same manner as in embodiment 1 except that the
15 heating process of the undercoating film is not conducted.

The surface roughness (Ra) shows a high value at 0.7 nm, and the initial critical inclination angle was also high at 23°. The contact angle is 108°, however, it went
20 down to 45° after the abrasion test.

Completing the results of the embodiments and comparisons mentioned heretofore, they are arranged and shown in TABLE 1.

TABLE 1

	Ingredients for Under- coating Treatment (Concentration n wt%)	Agent for Water Repellent Treatment	Appearance	Surface Rough- ness Ra (nm)	Initial Contact Angle (°)	Initial Critical Inclination Angle (°)	Contact Angle (°) after Weather Resistance Test (400 H)	Contact Angle (°) after Abrasion Test (100 times)
Embodiment 1	SiCl ₄ /0.01	agent a	OK	0.4	108	13	82	84
Comparison 1	SiCl ₄ /0.005	agent a	OK	0.9	107	18	71	65
Embodiment 2	SiCl ₄ /0.5	agent a	OK	0.2	107	12	86	82
Embodiment 3	SiCl ₄ /1.0	agent a	OK	0.3	108	12	87	87
Embodiment 2	SiCl ₄ /3.0	agent a	OK	0.2	109	13	86	87
Comparison 2	SiCl ₄ /5.0	agent a	remarkable reflection color	0.3	107	12	87	84
Embodiment 5	SiCl ₄ /0.5	agent b	OK	0.2	108	12	88	86
Comparison 3	SiCl ₄ /1.0	agent b	OK	0.7	106	18	65	80
Comparison 4	SiCl ₄ /1.0	agent b	OK	0.6	106	19	64	83
Comparison 5	SiCl ₄ /1.0*1	agent a	OK	0.8	107	20	63	67
Comparison 6	SiCl ₄ /1.0*2	agent a	OK	7.0	107	25	60	65
Comparison 7	TEOS/0.4	agent a	OK	0.7	107	22	54	67
Comparison 8	TEOS/0.4	agent a	OK	0.7	108	23	50	45

*1 solvent: Chloroform *2 solvent: perfluorocarbon

Ra was measured based on the standard of JIS B 0601-1982

As is fully explained in the above, in accordance with the substrate and the treating method of the present invention, since a highly reactive compound including chlorosilil radical in molecular form thereof is used as the liquid for the undercoating treatment, there is no necessity for conducting the baking at high temperature after forming the undercoating film layer. As a result, no large-scaled equipment is necessitated, and the production cost can be reduced.

Further, since it is sufficient for the agent for the undercoating treatment to be painted without using a liquid phase absorption or gaseous phase absorption method, the time for the treating can be shortened, and by using a low-cost alcohol solvent, the liquid for the undercoating treatment can be painted uniformly and thinly.

INDUSTRIAL APPLICABILITY

A substrate having a treatment surface according to the present invention is contributive to the water repellent or oil repellent window shield of the motor vehicle.

CLAIMS

1. A substrate having a processed surface, characterized in that, on a surface of said substrate formed of glass, ceramics, plastics or metal, an undercoating film layer is formed by drying a liquid for undercoating treatment which is obtained by dissolving and reacting a materiel having chlorosilil radical in molecular form therein within a alcohol group solvent, and further characterized in that on said undercoating film layer there is formed a water repellent or oil repellent layer, and that a surface roughness (Ra) of said surface layer is equal to or less than 0.5 nm.
2. A substrate having a processed surface as defined in Claim 1, further characterized in that a concentration of said materiel having chlorosilil radical in molecular form therein contained in said liquid for undercoating treatment is equal to or greater than 0.01 wt% and equal to or less than 3.0 wt%.
3. A substrate having a processed surface as defined in Claim 1, further characterized in that a concentration of said materiel having chlorosilil radical in molecular form therein contained in said undercoating treatment liquid is equal to or greater than 0.03 wt% and equal to or less than 1.0 wt%.
4. A substrate having a processed surface as defined in one of Claims 1 to 3, further characterized in that said materiel having chlorosilil radical in molecular form therein contained in said liquid for undercoating treatment includes at least one of SiCl_4 , SiHCl_3 and SiH_2Cl_2 .

5. A substrate having a processed surface as defined in one of Claims 1 to 4, further characterized in that the surface of said substrate on which said undercoating film layer is formed active surface by grinding and
5 cleaning to a surface roughness (Ra) of around from 0.5 nm to 3.0 nm.

6. A surface treating method for a substrate, characterized by coating an undercoating film layer comprised of a liquid for undercoating treatment, which
10 is obtained by dissolving and reacting a materiel having chlorosilil radical in molecular form therein within an alcohol group solvent, on a surface of a substrate of glass, ceramics, plastics or metal; drying said coated liquid for undercoating treatment; and thereafter
15 performing a surface treatment for forming a water repellent or oil repellent surface thereon without baking.

INTERNATIONAL SEARCH REPORT

Intern. Appl. No.

PCT/JP 98/01001

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C03C17/42 C09K3/18

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C03C C09K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	<p>EP 0 545 201 A (PPG INDUSTRIES INC) 9 June 1993 cited in the application see page 4, line 14 see page 5, line 3 - line 4 see page 6, line 23 - line 26 see page 6, line 55 - line 57 see page 7, line 37 see page 8, line 14 - line 16 see page 8, line 48 - line 50 see page 9, line 23 - line 26 see page 9, line 47 - line 48 see page 10, line 15 - line 20 see page 10, line 49 - line 50 see page 11, line 21 see examples 1,2,5,6,8-12 & JP 02 525 536 B</p> <p style="text-align: center;">---</p> <p style="text-align: center;">-/--</p>	1-6

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search

26 June 1998

Date of mailing of the international search report

08/07/1998

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Somann, K

INTERNATIONAL SEARCH REPORT

Inter. Appl. No.

PCT/JP 98/01001

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	<p>EP 0 484 746 A (MATSUSHITA ELECTRIC IND CO LTD) 13 May 1992 cited in the application see page 3, line 51 - page 4, line 12 see page 4, line 36 - line 37 see page 6, line 49 see page 8, line 36 see page 12, line 13 see page 12, line 47 see page 13, line 19 see page 13, line 54 see examples & JP 05 086 353 A</p>	1-6
Y	<p>WO 96 06895 A (XAAR LTD ;GRIFFIN MARY CATHERINE AMBROSE (GB); HOWARTH LESLIE GEOR) 7 March 1996 see examples 1,9-11</p>	1-6
A	<p>US 5 550 184 A (HALLING ROBERT A) 27 August 1996 see column 1, line 6 - line 15 see column 2, line 29 - column 3, line 6 see column 3, line 59 - column 4, line 42 see column 5, line 19 - column 6, line 6 see column 6, line 24 - line 55 see example 4</p>	1-6
A	<p>US 5 552 476 A (HALLING ROBERT A) 3 September 1996 see column 1, line 12 - line 20 see column 3, line 47 - column 4, line 8 see column 5, line 5 - line 7 see column 1, line 66 - column 2, line 16</p>	1-6
A	<p>US 5 459 198 A (SHARP KENNETH G) 17 October 1995 see column 1, line 9 - line 11 see column 2, line 32 - line 47 see column 7, line 9 - line 41</p>	1-6
A	<p>EP 0 547 550 A (MATSUSHITA ELECTRIC IND CO LTD) 23 June 1993 cited in the application see page 6, line 42 - line 53 see examples & JP 05 161 844 A</p>	1-6

-/--

INTERNATIONAL SEARCH REPORT

Inter. Jnal Application No

PCT/JP 98/01001

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>DATABASE WPI Section Ch, Week 9218 Derwent Publications Ltd., London, GB; Class A82, AN 85-090552 XP002069396 & JP 04 020 781 B (ASAHI GLASS CO LTD) cited in the application see abstract</p> <p style="text-align: center;">----</p>	1-6
A	<p>PATENT ABSTRACTS OF JAPAN vol. 015, no. 100 (C-0813), 11 March 1991 & JP 02 311332 A (SEKISUI CHEM CO LTD), 26 December 1990, cited in the application see abstract see line 1</p> <p style="text-align: center;">-----</p>	1-6

INTERNATIONAL SEARCH REPORT

Information on patent family members

Inter. Appl. No.

PCT/JP 98/01001

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 0545201 A	09-06-1993	US 5328768 A CA 2082094 A,C JP 2525536 B JP 5238781 A	12-07-1994 30-05-1993 21-08-1996 17-09-1993
EP 0484746 A	13-05-1992	JP 2052440 C JP 4252235 A JP 7091402 B JP 2501248 B JP 4239635 A JP 2093588 C JP 4240171 A JP 8009510 B JP 4256710 A JP 7098026 B CA 2054094 A DE 69122212 D DE 69122212 T KR 9504153 B US 5380585 A US 5466486 A JP 5086353 A DE 69120788 D DE 69120788 T EP 0493747 A JP 5070761 A KR 9615626 B US 5407709 A US 5284707 A	10-05-1996 08-09-1992 04-10-1995 29-05-1996 27-08-1992 18-09-1996 27-08-1992 31-01-1996 11-09-1992 25-10-1995 26-04-1992 24-10-1996 30-01-1997 27-04-1995 10-01-1995 14-11-1995 06-04-1993 14-08-1996 07-11-1996 08-07-1992 23-03-1993 18-11-1996 18-04-1995 08-02-1994
WO 9606895 A	07-03-1996	CA 2198720 A EP 0778869 A	07-03-1996 18-06-1997
US 5550184 A	27-08-1996	AU 1937695 A EP 0748323 A JP 9509939 T WO 9523804 A US 5552476 A	18-09-1995 18-12-1996 07-10-1997 08-09-1995 03-09-1996
US 5552476 A	03-09-1996	US 5550184 A	27-08-1996

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/JP 98/01001

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 5552476 A		AU 1937695 A EP 0748323 A JP 9509939 T WO 9523804 A	18-09-1995 18-12-1996 07-10-1997 08-09-1995
US 5459198 A	17-10-1995	AU 2967995 A CA 2192551 A EP 0772644 A JP 10503795 T WO 9604331 A	04-03-1996 15-02-1996 14-05-1997 07-04-1998 15-02-1996
EP 0547550 A	23-06-1993	JP 2603017 B JP 5161844 A JP 5168913 A DE 69224888 D KR 9701519 B US 5372851 A	23-04-1997 29-06-1993 02-07-1993 30-04-1998 11-02-1997 13-12-1994